

# Ab initio variational solution for lattice thermal conductivity in diamond

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We present a first-principles theoretical approach for evaluating the lattice thermal conductivity based on the exact solution of the Boltzmann transport equation. We use the variational principle and the conjugate gradient scheme, which provide us with an algorithm faster than the one previously used in literature and able to always convergence to the exact solution. Three-phonon normal and umklapp collision, isotope scattering and border effects are rigorously treated in the calculation. Good agreement with experimental data for diamond is found. Moreover we show that that by growing more enriched diamond samples it is possible to achieve values of thermal conductivity up to three times larger than the commonly observed in isotopically enriched diamond samples with 99.93%  $C^{12}$  and 0.07  $C^{13}$ .

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## I. INTRODUCTION

Thermal conductivity is one of the most important parameter used to characterize transport phenomena in solid state systems. A predictive theory for evaluating thermal conductivity is essential for the design of new materials for efficient thermoelectric refrigeration and power generation<sup>1</sup> and it could help in understanding heat dissipation in micro- and nano-electronics devices.<sup>2</sup>

When heat is mostly carried by lattice vibrations, such as in semiconductors and insulators, a correct theoretical prediction of thermal transport properties cannot leave aside an accurate description of the phonon-phonon interactions and lifetimes. These quantities are related to second and third order derivatives of the ground state energy with respect to atomic displacements. Specifically the harmonic interatomic force constants determine phonon frequencies, group velocities and phonon populations while the anharmonic interatomic force constants determine phonon scattering rates and linewidths.

A first microscopic description of the thermal conductivity in semiconductors and insulators has been formulated in 1929 by Peierls and it has became known as Boltzmann Transport Equation (BTE). This equation involves the unknown perturbed population of a phonon mode and it describes how the perturbation due to a gradient of temperature is balanced by the change in the phonon population due to the scattering processes. A good predictive theory requires then a good knowledge of i) the harmonic and anharmonic inter-atomic force constants (IFCs) and ii) the perturbed phonon population obtained as solution of the BTE.

Both these issues have non trivial solutions. The first issue can be addressed in the framework of Density Functional Perturbation Theory (DFPT) evaluating the interatomic force constants fully ab initio using the “2n+1” theorem<sup>3-5</sup>. An efficient implementation of this method extended for metallic systems exist in the Quantum ESPRESSO package<sup>6</sup> for zone-centered mode<sup>4</sup>.

A generalization for metallic systems and arbitrary phonons has recently been developed and implemented in the the Quantum-ESPRESSO package<sup>7</sup>.

The second issue, lying in solving the BTE equation exactly, is due to the complexity of the scattering term. The change in the phonon population numbers of each single state involved in the scattering term depend in turn, on the change in the occupation number of the other states involved.

Several theoretical studies instead of attempting to solve the BTE employ a common approximation, namely the single mode phonon relaxation time approximation (SMA)<sup>8-10</sup>. This approximation describes rigorously the depopulation of the phonon states but not the corresponding repopulation, which is assumed to have no memory of the initial phonon distribution. The momentum conserving character of the normal (N) processes gives then rise to a conceptual inadequacy of the SMA description and its use becomes questionable in particular in the range of low temperatures where the umklapp (U) processes are frozen out and N processes lead the phonon relaxation<sup>11</sup>.

Improved approximate techniques involve the use of a variational procedure<sup>12,13</sup>. In such a kind of approach, originally introduced by Hamilton and Parrott<sup>14</sup>, the thermal conductivity is found by variationally optimizing a trial function adopted for describing the non-equilibrium phonon distribution function. Unfortunately the less the system is symmetric and isotropic the more the result and the accuracy will be affected by the form adopted for the trial function.

A first approach to solve exactly the linearized BTE has been introduced in the 90s by Omini and Sparavigna<sup>15</sup>. The numerical solution evaluated on a discrete grid is obtained via a self-consistent iterative procedure, but as indicated by the authors<sup>15</sup> there is not a general proof that convergence will always be obtained with this approach. Nevertheless until now the Omini Sparavigna iterative procedure had represented the unique numerically exact method used to solve the BTE and

evaluating the thermal conductivity<sup>16–21</sup>.

In this paper we present a new numerical approach for solving exactly the linearized BTE. This method joins together the variational principle and the resolution on a discrete grid. More specifically by using the variational principle and the conjugate gradient method we present a stable algorithm, faster than the one previously proposed and able to always converge to the exact solution. As a first application we use this algorithm for studying the lattice thermal conductivity in naturally occurring and isotopically enriched diamond. We find a good agreement with experiments and we are able to give for the first time a theoretical limit based on the exact solution of the BTE of the maximum lattice thermal conductivity reachable in isotopically pure diamond samples.

## II. BOLTZMANN TRANSPORT EQUATION

When a gradient of temperature  $\nabla T$  is established in a system a subsequent heat flux will start propagating in the medium. Without loss of generality we assume that the gradient of temperature is along the direction  $x$ . The flux of heat, collinear to the temperature gradient, can be written in terms of phonon energies  $\hbar\omega_{\mathbf{q}j}$  phonon group velocities  $c_{\mathbf{q}j}$  in the  $x$  direction and the perturbed phonon population  $n_{\mathbf{q}j}$ .

$$\frac{1}{N_0\Omega} \sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j} c_{\mathbf{q}j} n_{\mathbf{q}j} = -k \frac{\partial T}{\partial x} \quad (1)$$

in the l.h.s  $\omega_{\mathbf{q}j}$  is the pulsation of the phonon mode with vector  $\mathbf{q}$  and branch index  $j$ ,  $\Omega$  is the volume of the unit cell and the sum runs over a uniform mesh of  $N_0$   $\mathbf{q}$  points. While in the r.h.s.  $k$  is the diagonal component of the thermal conductivity in the temperature-gradient direction. Knowledge of the phonon perturbed population allows heat flux and subsequently thermal conductivity to be evaluated.

Unlike phonon scattering by defects, impurities and boundaries the anharmonic scattering represents an intrinsic resistive process and in high quality samples it dominates the behaviour of lattice thermal conductivity at room temperature balancing the perturbation due to the gradient of temperature. The balance equation, namely the Boltzmann Transport Equation (BTE), formulated in 1929 by Peierls<sup>22</sup> is:

$$-c_{\mathbf{q}j} \frac{\partial T}{\partial x} \left( \frac{\partial n_{\mathbf{q}j}}{\partial T} \right) + \left. \frac{\partial n_{\mathbf{q}j}}{\partial t} \right|_{scatt} = 0 \quad (2)$$

with the first term indicating the phonon diffusion due to the temperature gradient and the second term the scattering rate due to all the scattering processes. This equation has to be solved self consistently. In the general approach<sup>10</sup>, for small perturbation from the equilibrium, the temperature gradient of the perturbed phonon population is replaced with the temperature gradient of

the equilibrium phonon population  $\partial n_{\mathbf{q}j}/\partial T = \partial \bar{n}_{\mathbf{q}j}/\partial T$  where  $\bar{n}_{\mathbf{q}j} = (e^{\hbar\omega_{\mathbf{q}j}/K_B T} + 1)^{-1}$ ; while for the scattering term it can be expanded about its equilibrium value in terms of a first order perturbation:

$$n_{\mathbf{q}j} \simeq \bar{n}_{\mathbf{q}j} + \bar{n}_{\mathbf{q}j} (\bar{n}_{\mathbf{q}j} + 1) \frac{\partial T}{\partial x} f_{\mathbf{q}j}^{\text{EX}} \quad (3)$$

The linearized BTE can be then written in the following form<sup>23</sup>:

$$\begin{aligned} -c_{\mathbf{q}j} \left( \frac{\partial \bar{n}_{\mathbf{q}j}}{\partial T} \right) = & \sum_{\mathbf{q}'j', \mathbf{q}''j''} \left[ P_{\mathbf{q}j, \mathbf{q}'j'}^{\mathbf{q}''j''} (f_{\mathbf{q}j}^{\text{EX}} + f_{\mathbf{q}'j'}^{\text{EX}} - f_{\mathbf{q}''j''}^{\text{EX}}) \right. \\ & + \frac{1}{2} P_{\mathbf{q}j}^{\mathbf{q}'j', \mathbf{q}''j''} (f_{\mathbf{q}j}^{\text{EX}} - f_{\mathbf{q}'j'}^{\text{EX}} - f_{\mathbf{q}''j''}^{\text{EX}}) \Big] \\ & + \sum_{\mathbf{q}'j'} P_{\mathbf{q}j, \mathbf{q}'j'}^{\text{isot}} (f_{\mathbf{q}j}^{\text{EX}} - f_{\mathbf{q}'j'}^{\text{EX}}) \\ & + P_{\mathbf{q}j}^{\text{be}} f_{\mathbf{q}j}^{\text{EX}} \end{aligned} \quad (4)$$

where the sum on  $\mathbf{q}'$  and  $\mathbf{q}''$  is performed in the Brillouin Zone (BZ). The EX superscript denotes the exact solution on the BTE, to be distinguished to the approximated solutions we will discuss later.

In Eq. 4 the anharmonic scattering processes as well as the scattering with the isotopic impurities and the border effect are considered. More specifically (see Fig.1)  $P_{\mathbf{q}j, \mathbf{q}'j'}^{\mathbf{q}''j''}$  is the scattering rate at the equilibrium of a processes where a phonon mode  $\mathbf{q}j$  scatters by absorbing another mode  $\mathbf{q}'j'$  to generate a third phonon mode  $\mathbf{q}''j''$ . While  $P_{\mathbf{q}j}^{\mathbf{q}'j', \mathbf{q}''j''}$  is the scattering rate at the equilibrium of a process where a phonon mode  $\mathbf{q}j$  decays in two modes  $\mathbf{q}'j'$  and  $\mathbf{q}''j''$ .

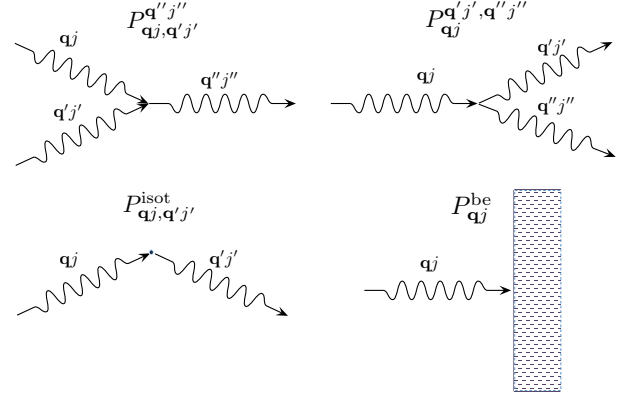


Figure 1. Phonon scattering processes in a finite size anharmonic crystal in presence of isotopic impurities.

The two scattering rates have the forms:

$$\begin{aligned} P_{\mathbf{q}j, \mathbf{q}'j'}^{\mathbf{q}''j''} = & \frac{2\pi}{N_0\hbar^2} \sum_{\mathbf{G}} |V^{(3)}(\mathbf{q}j, \mathbf{q}'j', -\mathbf{q}''j'')|^2 \\ & \bar{n}_{\mathbf{q}j} \bar{n}_{\mathbf{q}'j'} (\bar{n}_{\mathbf{q}''j''} + 1) \delta_{\mathbf{q}+\mathbf{q}'-\mathbf{q}'', \mathbf{G}} \\ & \delta(\hbar\omega_{\mathbf{q}j} + \hbar\omega_{\mathbf{q}'j'} - \hbar\omega_{\mathbf{q}''j''}) \end{aligned} \quad (5)$$

$$P_{\mathbf{q}j}^{\mathbf{q}'j', \mathbf{q}''j''} = \frac{2\pi}{N_0 \hbar^2} \sum_{\mathbf{G}} |V^{(3)}(\mathbf{q}j, -\mathbf{q}'j', -\mathbf{q}''j'')|^2 \frac{\bar{n}_{\mathbf{q}j}(\bar{n}_{\mathbf{q}'j'}+1)(\bar{n}_{\mathbf{q}''j''}+1)\delta_{\mathbf{q}-\mathbf{q}'-\mathbf{q}'', \mathbf{G}}}{\delta(\hbar\omega_{\mathbf{q}j} - \hbar\omega_{\mathbf{q}'j'} - \hbar\omega_{\mathbf{q}''j''})} \quad (6)$$

with  $\mathbf{G}$  the reciprocal lattice vectors. In order to evaluate them it is necessary to compute the third derivative  $V^{(3)}$  of the total energy of the crystal  $\mathcal{E}^{tot}(\{u_{s\alpha}(\mathbf{R}_l)\})$ , with respect to the atomic displacement  $u_{s\alpha}(\mathbf{R}_l)$ , from the equilibrium position, of the  $s$ -th atom, along the  $\alpha$  Cartesian coordinate in the crystal cell identified by the lattice vector  $\mathbf{R}_l$  :

$$V^{(3)}(\mathbf{q}j, \mathbf{q}'j', \mathbf{q}''j'') = \frac{\partial^3 \mathcal{E}^{cell}}{\partial X_{\mathbf{q}j}, \partial X_{\mathbf{q}'j'}, \partial X_{\mathbf{q}''j''}} \quad (7)$$

where  $\mathcal{E}^{cell}$  is the energy per unit cell and the adimensional quantity  $X_{\mathbf{q}j}$  is defined by

$$X_{\mathbf{q}j} = \frac{1}{N_0} \sum_{l, s, \alpha} \sqrt{\frac{2M_s \omega_{\mathbf{q}j}}{\hbar}} z_{\mathbf{q}j}^{s\alpha*} u_{s\alpha}(\mathbf{R}_l) e^{-i\mathbf{q} \cdot \mathbf{R}_l} \quad (8)$$

$z_{\mathbf{q}j}^{s\alpha}$  being the orthogonal phonon eigenmodes normalized on the unit cell and  $M_s$  the atomic masses.

The rate of the elastic scattering with isotopic impurities (see Fig.1) has the form<sup>24</sup>:

$$P_{\mathbf{q}j, \mathbf{q}'j'}^{\text{isot}} = \frac{\pi}{2N_0} \omega_{\mathbf{q}j} \omega_{\mathbf{q}'j'} \left[ \bar{n}_{\mathbf{q}j} \bar{n}_{\mathbf{q}'j'} + \frac{\bar{n}_{\mathbf{q}j} + \bar{n}_{\mathbf{q}'j'}}{2} \right] \sum_s g_2^s \left| \sum_{\alpha} z_{\mathbf{q}j}^{s\alpha*} \cdot z_{\mathbf{q}'j'}^{s\alpha} \right|^2 \delta(\omega_{\mathbf{q}j} - \omega_{\mathbf{q}'j'}) \quad (9)$$

where  $g_2^s = \frac{(M_s - \langle M_s \rangle)^2}{\langle M_s \rangle^2}$  is the average on the mass distribution of the atom of type  $s$ . In presence of two isotopes  $M_s$  and  $M_{s'}$  it can be written in terms of the concentration  $\epsilon$  and mass change  $\Delta M_s = M_{s'} - M_s$  :

$$g_2^s = \epsilon(1 - \epsilon) \frac{|\Delta M_s|}{\langle M_s \rangle} \quad (10)$$

with  $\langle M_s \rangle = M_s + \epsilon \Delta M_s$ .

Eventually, in system of finite size,  $P_{\mathbf{q}j}^{\text{be}}$  describes the absorption of phonon on the border (see Fig.1):

$$P_{\mathbf{q}j}^{\text{be}} = \frac{c_{\mathbf{q}j}}{LF} \bar{n}_{\mathbf{q}j} (\bar{n}_{\mathbf{q}j} + 1) \quad (11)$$

where  $L$  is the Casimir length of the sample and  $F$  a correction factor depending on the width to length ratio of the sample.

For the sake of clarity we will contract from now on the vector  $\mathbf{q}$  and branch index  $j$  in one single mode index  $\nu$ . The BTE of Eq. 4 can be written as a linear system in a matrix form:

$$\mathbf{A} \mathbf{f}^{\text{EX}} = \mathbf{b} \quad (12)$$

with the vector  $b_{\nu'} = -c_{\nu'} \hbar \omega_{\nu'} \bar{n}_{\nu'} (\bar{n}_{\nu'} + 1)$  and the matrix

$$A_{\nu, \nu'} = \left[ \sum_{\nu'', \nu'''} \left( P_{\nu, \nu'''}^{\nu''} + \frac{P_{\nu'', \nu'''}^{\nu}}{2} \right) + \sum_{\nu''} P_{\nu, \nu''}^{\text{isot}} + P_{\nu}^{\text{be}} \right] \delta_{\nu, \nu'} + \sum_{\nu''} \left( P_{\nu, \nu''}^{\nu'} - P_{\nu, \nu''}^{\nu''} + P_{\nu', \nu''}^{\nu} \right) + P_{\nu, \nu'}^{\text{isot}} \quad (13)$$

where we have used  $P_{\nu'}^{\nu', \nu''} = P_{\nu', \nu''}^{\nu'}$  from the detailed balance condition  $\bar{n}_{\nu'} (\bar{n}_{\nu''} + 1) (\bar{n}_{\nu'} + 1) = (\bar{n}_{\nu'} + 1) \bar{n}_{\nu'} \bar{n}_{\nu''}$  (valid under the assumption  $\hbar\omega = \hbar\omega' + \hbar\omega''$ ). In this form the matrix is symmetric and positive semi-definite (see Appendix A for demonstrations) and it can be decomposed in  $\mathbf{A} = \mathbf{A}^{\text{out}} + \mathbf{A}^{\text{in}}$ , where

$$A_{\nu, \nu'}^{\text{out}} = \frac{\bar{n}_{\nu} (\bar{n}_{\nu'} + 1)}{\tau_{\nu}^{\text{T}}} \delta_{\nu, \nu'} \quad (14)$$

$$A_{\nu, \nu'}^{\text{in}} = - \sum_{\nu''} \left( P_{\nu, \nu''}^{\nu'} - P_{\nu, \nu''}^{\nu''} + P_{\nu', \nu''}^{\nu} \right) + P_{\nu, \nu'}^{\text{isot}} \quad (15)$$

$\tau_{\nu}^{\text{T}}$  being the phonon relaxation time (see Appendix B). The  $\mathbf{A}^{\text{out}}$  diagonal matrix describes the depopulation of phonon states due to the scattering mechanisms while the  $\mathbf{A}^{\text{in}}$  matrix describes their repopulation due to the incoming output phonons.

The solution of the linear system in Eq. 12 is obtained formally by inverting the matrix  $\mathbf{A}$ .

$$\mathbf{f}^{\text{EX}} = \frac{1}{\mathbf{A}} \mathbf{b} \quad (16)$$

and subsequently the thermal conductivity will be evaluated as:

$$k = \lambda \mathbf{b} \cdot \mathbf{f}^{\text{EX}} \quad (17)$$

with  $\lambda = \hbar / N_0 \Omega k_B T^2$ .

### III. SOLUTIONS OF THE BOLTZMANN TRANSPORT EQUATION

The complexity of the BTE lies in the need of explicitly computing, storing and inverting the large matrix  $\mathbf{A}$ . In the SMA the BTE is solved for the  $n_{\nu}$  neglecting the role of the repopulation by means setting  $\mathbf{A}^{\text{in}}$  to zero.

$$\mathbf{f}^{\text{SMA}} = \frac{1}{\mathbf{A}^{\text{out}}} \mathbf{b}. \quad (18)$$

Storing and inverting  $\mathbf{A}^{\text{out}}$  is trivial due to its diagonal form. The lattice thermal conductivity in SMA is then

$$k^{\text{SMA}} = \lambda \mathbf{b} \cdot \mathbf{f}^{\text{SMA}} = \frac{\hbar^2}{N_0 \Omega k_B T^2} \sum_{\nu} c_{\nu}^2 \omega_{\nu}^2 \bar{n}_{\nu} (\bar{n}_{\nu} + 1) \tau_{\nu}^{\text{T}} \quad (19)$$

Such approximation is exact if the repopulation loses memory of the initial phonon distribution and if it is

proportional to the equilibrium population of  $\nu$ . It remains anyway a good approximation if the repopulation is isotropic. An exact solution of Eq. 12, that does not imply neither storing nor the explicit inversion of matrix  $\mathbf{A}$ , has been proposed by Omini and Sparavigna (OS)<sup>16</sup> by converging with respect to the iteration  $i$  the following:

$$\mathbf{f}_{i+1} = \frac{1}{\mathbf{A}^{\text{out}}} \mathbf{b} - \frac{1}{\mathbf{A}^{\text{out}}} \mathbf{A}^{\text{in}} \mathbf{f}_i \quad (20)$$

with the iteration zero consisting in the SMA  $\mathbf{f}_0 = \mathbf{f}^{\text{SMA}}$ . This procedure required, as for the SMA, only the trivial inversion of the diagonal matrix  $\mathbf{A}^{\text{out}}$ . Instead of storing and inverting  $\mathbf{A}$ , it just requires the evaluation of  $\mathbf{A}^{\text{in}} \mathbf{f}_i$ , which is an operation computationally much less demanding, at each iteration  $i$  of the OS method. Once the convergence is obtained the thermal conductivity is evaluated by :

$$k^{\text{NV}}(\mathbf{f}_i) = \lambda \mathbf{b} \cdot \mathbf{f}_i \quad (21)$$

From a mathematical point of views the OS iterative procedure can be written as a geometric series:

$$\mathbf{f}_i = \sum_{j=0,i} \left( -\frac{1}{\mathbf{A}^{\text{out}}} \mathbf{A}^{\text{in}} \right)^j \frac{1}{\mathbf{A}^{\text{out}}} \mathbf{b} \quad (22)$$

that means that only if the absolute value of the ratio  $(\mathbf{A}^{\text{out}^{-1}} \mathbf{A}^{\text{in}})$  is smaller than one it is possible to reach a converged solution of the linear system in Eq. 12 .

An alternative approach consists in observing that due to the properties of the matrix  $\mathbf{A}$  (see Appendix A) it is possible to find the exact solution of the linearized BTE, Eq.12, by using the variational principle. Indeed the solution of the BTE is the vector  $\mathbf{f}^{\text{EX}}$  which makes stationary the quadratic form<sup>9,14</sup>

$$\mathcal{F}(\mathbf{f}) = \frac{1}{2} \mathbf{f} \cdot \mathbf{A} \mathbf{f} - \mathbf{b} \cdot \mathbf{f} \quad (23)$$

Since  $\mathbf{A}$  is positive the stationary point is the global and single minimum of this functional. One can then define a variational conductivity functional:

$$k^{\text{V}}(\mathbf{f}) = -2\lambda \mathcal{F}(\mathbf{f}) \quad (24)$$

that has the property  $k^{\text{V}}(\mathbf{f}^{\text{EX}}) = k$  while any other value of  $k^{\text{V}}(\mathbf{f})$  underestimates  $k$ . In other words to find the minimum of the quadratic form it is equivalent to maximize the thermal conductivity functional. As a consequence an error  $\delta \mathbf{f} = \mathbf{f} - \mathbf{f}^{\text{EX}}$  results in an error in conductivity, linear in  $\delta \mathbf{f}$  if the functional is written in Eq. 21 form, and quadratic if the variational form (Eq. 24) is used.

In literature<sup>14</sup>, due to the complexity of the numerical calculations the variational scheme was used together with a trial function for describing the non equilibrium phonon distribution function affecting then the accuracy

of the final result with the form of the specific probe function chosen. In our scheme we avoid the use of trial function and we solve Eq. 12 on a grid (as in OS procedure) by using the conjugate gradient method<sup>25</sup>, as reported in Appendix C, to obtain the exact solution of the BTE equation. In order to speed up the convergence of the conjugate gradient we take advantage of the diagonal and dominant role of  $\mathbf{A}^{\text{out}}$  and we use a preconditioned conjugate gradient. Formally, this corresponds to use in the minimization the rescaled variable:

$$\tilde{\mathbf{f}} = \sqrt{\mathbf{A}^{\text{out}}} \mathbf{f} \quad (25)$$

and then, with respect to this new variable, minimize the quadratic form  $\tilde{\mathcal{F}}(\tilde{\mathbf{f}}) = \mathcal{F}(\mathbf{f})$  where:

$$\tilde{\mathcal{F}}(\tilde{\mathbf{f}}) = \frac{1}{2} \tilde{\mathbf{f}} \cdot \tilde{\mathbf{A}} \tilde{\mathbf{f}} - \tilde{\mathbf{b}} \cdot \tilde{\mathbf{f}} \quad (26)$$

and

$$\tilde{\mathbf{A}} = \frac{1}{\sqrt{\mathbf{A}^{\text{out}}}} \mathbf{A} \frac{1}{\sqrt{\mathbf{A}^{\text{out}}}} \quad (27)$$

$$\tilde{\mathbf{b}} = \frac{1}{\sqrt{\mathbf{A}^{\text{out}}}} \mathbf{b} \quad (28)$$

Notice that  $\tilde{\mathbf{f}}^{\text{SMA}} = \tilde{\mathbf{b}}$ . The square root evaluation of  $\mathbf{A}^{\text{out}}$  is trivial due to its diagonal form. The computational cost per iteration of the conjugate gradient scheme is equivalent to the OS one, but it always converges and requires a smaller number of iterations.

#### IV. COMPUTATIONAL DETAILS

In order to compute the thermal conductivity the only input required are the second and third order IFCs. Both of them were calculated by using the Quantum ESPRESSO package<sup>6</sup> following the method explained in<sup>7</sup>. The first BZ is discretized into a uniform grid centered at Gamma of  $\mathbf{q}$  points. In such a way that if  $\mathbf{q}$  and  $\mathbf{q}'$  belong to the mesh also  $\mathbf{q} \pm \mathbf{q}'$  belongs to the mesh, assuring a perfect momentum conservation. At any  $\mathbf{q}$  the phonon frequencies are evaluated from the second order force constants and the phonon group velocities are computed from the derivative of the phonon dispersion  $\partial \omega / \partial \mathbf{q}$ , using the Hellman-Feynmann theorem and obtaining the following velocity matrix directly from the Dynamical matrix  $\mathcal{D}$ :

$$C_{jj'} = \sum_{\alpha \alpha' s s'} \frac{1}{2\sqrt{M_s M_{s'} \omega_{\mathbf{qj}}}} z_{\mathbf{qj}}^{s\alpha*} \frac{\partial \mathcal{D}_{ss'}^{\alpha \alpha'}}{\partial q_x} z_{\mathbf{qj}'}^{s' \alpha'} \quad (29)$$

In the non degenerate case  $c_{\mathbf{qj}} = C_{jj}$  while in the degenerate one we use the phonon polarization vectors that diagonalize the matrix in the degenerate subspace. To compute the scattering rates, the BZ is again discretized into a grid of  $\mathbf{q}'$  points centered in zero. The delta function for the energy conservation is replaced by a Gaussian

$$\delta(\hbar\omega) = \frac{1}{\sqrt{\pi}\sigma} \exp(-(\hbar\omega/\sigma)^2). \quad (30)$$

It is important to notice that when the delta function is substituted with a Gaussian the detailed balance condition is only valid under approximation. This means that the OS definition of matrix  $\mathbf{A}$  given in<sup>16</sup> and our definition, in Eq. 13, are not equivalent anymore. Our definition has the advantage to keep, for any finite  $\sigma$ ) in Eq. 30, the symmetric and non-negative character of the  $\mathbf{A}$  matrix thanks to the symmetric definition of the scattering rate with the isotopic impurities given in Eq. 9 and the replacement of  $P_{\nu'}^{\nu}, \nu''$  with  $P_{\nu', \nu''}^{\nu}$ .

For diamond calculations: a smearing  $\sigma = 20 \text{ cm}^{-1}$  along the  $\mathbf{q}'$  mesh of  $30 \times 30 \times 30$  has been found to lead to converged relaxation times and for the border effects: we used a Casimir length  $L = 0.3 \text{ cm}$  and a shape factor  $F = 0.5$ <sup>26,27</sup>.

A norm conserving pseudopotential<sup>28</sup> with cutoff radii of 1.2 a.u. and core correction has been used for C. The exchange correlation energy is calculated in the framework of the Local Density Approximation (LDA)<sup>29</sup>. A plane-wave kinetic energy cutoff of 90 Ry and of 360 Ry for the charge density. We used a  $8 \times 8 \times 8$  Monkhorst-Pack of the BZ for the electronic k-point sampling.

Anharmonic forces have been computed on a  $4 \times 4 \times 4$  q-point phonon grid on the BZ, Fourier interpolated with a finer  $30 \times 30 \times 30$  mesh for the Boltzmann calculations.

## V. RESULTS AND DISCUSSION

In Fig.2 a comparison between the convergence trend obtained via the OS iteration scheme or the conjugate gradient is reported for the case of bulk diamond at 100 K. The OS standard iterative scheme shows a numerical instability after 77 iterations. This instability prevents the scheme to approach the exact solution  $k$  with a precision higher than  $\sim 300 \text{ W m}^{-1} \text{ K}^{-1}$ . A higher precision is achievable with the Conj. Grad. already after 4 iterations. As expected, if the variational definition of  $k$  (Eq. 24) is used in the OS iterative scheme, half the number of iterations are necessary to reach the same precision and the numerical instability appears after 41 iterations. Moreover the convergence trend of the Conj. Grad. scheme without preconditioning is reported in the same graph to show how preconditioning is necessary to ensure a fast convergence.

We have chosen for the comparison a temperature of 100 K close to the maximum value of thermal conductivity obtainable in finite size diamond samples<sup>20,30,31</sup>. In this range of temperatures, where the U processes are a few and the border effects are not dominant, it is important to have a stable algorithm able to well characterize the few scattering processes that drive the lattice thermal conductivity in order to obtain the correct result.

Fig. 3a compares the lattice thermal conductivity of isotopically enriched and naturally occurring diamond obtained by solving exactly the BTE equation with the experimental results as a function of temperatures. The circles<sup>30</sup> and squares<sup>32</sup> pointers represent the measured

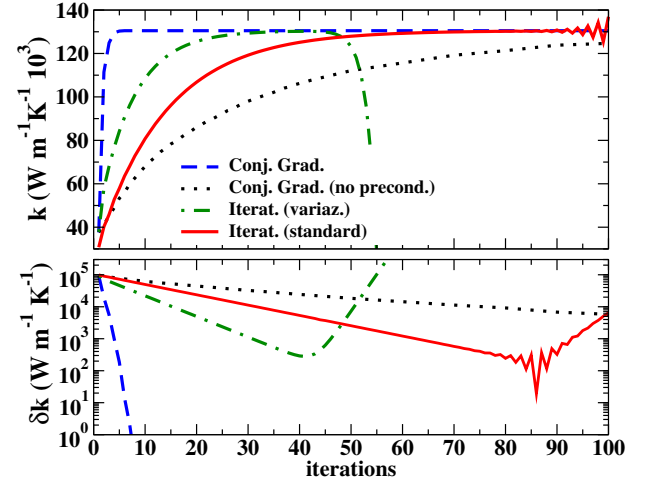


Figure 2. (Color online). Lattice thermal conductivity of diamond at 100 K (top panel) and absolute error  $\delta k$  (bottom panel) compared to the exact solution  $k$  for: the iterative scheme in the Omini Sparavigna standard definition (solid line), the iterative scheme in the variational definition given in Eq. 24 (dash-dotted line), and the conjugate gradient method with (dashed line) and without (dotted line) preconditioning, as a function of the order of iteration.

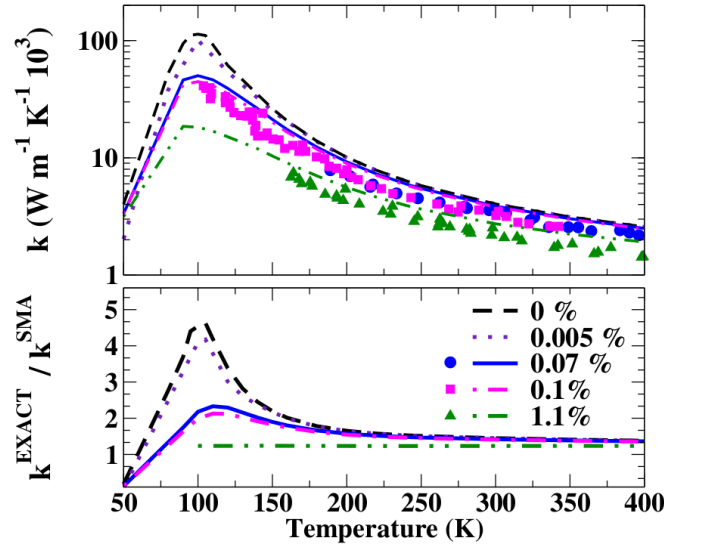


Figure 3. (Color online). Lattice thermal conductivity of isotopically enriched and naturally occurring diamond as a function of temperatures. (Top) Experimental values (circles<sup>30</sup>, squares<sup>32</sup> and triangles<sup>30</sup>) at different  $\text{C}^{13}$  percentages (0.07%, 0.1% and 1.1%) are compared with the results of our ab initio calculations (solid, dash-dotted and dash with two dots lines). As indication of the theoretical limit a dashed line for the case in total absence of  $\text{C}^{13}$  is reported. (Bottom) Ratio between the exact and the SMA solution as a function of temperature at different  $\text{C}^{13}$  percentages.

values for isotopically enriched diamond with 99.93%  $C^{12}$ , 0.07%  $C^{13}$  and 99.9%  $C^{12}$ , 0.1%  $C^{13}$  respectively. While the triangles<sup>30</sup> represent naturally occurring diamond with 98.9%  $C^{12}$  and 1.1%  $C^{13}$ . The results are in very good agreement. In the same picture is also indicated with a dashed line the thermal conductivity in total absence of  $C^{13}$ . This value gives a theoretical limit of the maximum lattice thermal conductivity reachable. In the picture it is easy to notice that at 100 K, where the lattice thermal conductivity takes its maximum values,  $k_{0\%C^{13}} \simeq 3k_{0.07\%C^{13}}$ . This means that there is still a significant increment in thermal conductivity achievable by growing more enriched diamond samples. As the temperature increases, the values for the naturally occurring and isotopically pure samples become indistinguishable. This is due to the U scattering becoming stronger and consequently driving the thermal conductivity as the temperature increases. For temperatures lower than 100 K the border effects become dominant.

Fig.3b shows the ratio between the thermal conductivity obtained by solving exactly BTE equation and by using the SMA as a function of temperatures (for  $T \geq 100$  K). The lower the temperature and the less the  $C^{13}$  abundance the bigger becomes the ratio between the exact solution and the SMA solution. In other words, the less are the events of scattering that do not conserve the momentum (i.e. Umklapp, isotopes and border scattering) the less the SMA is able to give a good description of the process. In Fig.3 is shown also the case with 99.995%  $C^{12}$  and 0.005%  $C^{13}$  as a further indication of how even small changes in the sample enrichment could give rise to sensible differences in the thermal transport properties of the material.

In Fig.4 this last concept is more enlightened. Diamond thermal conductivity is represented as a function of isotopic presence for two different temperature 100 K and 300 K. At  $T = 100$  K the range of thermal conductivity explores by changing the percentage of  $C^{13}$  from 0 to 1% spans one order of magnitude while at 300 K the differences between the different isotopic percentage becomes smaller with a ratio between the two extreme cases reduced of a factor 1.5.

## VI. CONCLUSIONS

In this paper we have presented a new numerical approach for solving exactly the linearized BTE. We have shown how joining the variational principle approach and the resolution on a grid it is possible to converge to the exact solution. Moreover the preconditioned conjugate gradient scheme with the line minimization assures a significant faster convergence than the method previously proposed by Omini and Sparavigna<sup>15</sup> with an equivalent computational cost per iteration.

As first application of our method we have then computed the lattice thermal conductivity of isotopically enriched and naturally occurring diamond by evaluating

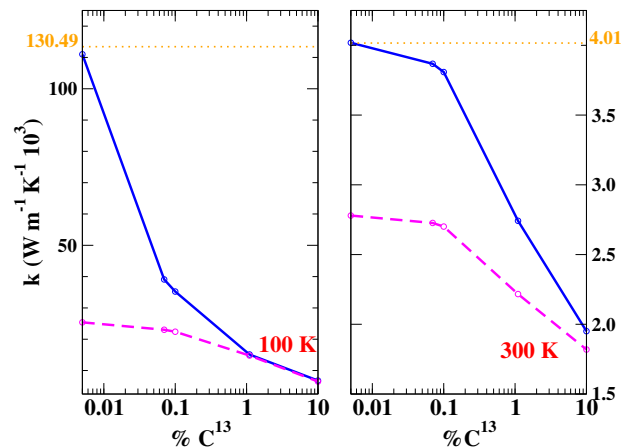


Figure 4. (Color online) Diamond lattice thermal conductivity as a function of isotopic presence at 100 K (left) and 300 K (right). The solid lines join the values obtained solving the BTE while the dashed lines join the SMA solutions. The value of the thermal conductivity in absolute absence of  $C^{13}$  in the two temperature cases is represented by a dotted horizontal line.

the harmonic and anharmonic IFCs fully ab initio in the framework of DFPT using a recent general implementation of the “2n+1” theorem in the Quantum ESPRESSO package combined with an exact solution of the linearized phonon BTE.

In agreement with what previously shown in literature<sup>20,26</sup> we have demonstrated the severe inadequacy of the commonly used SMA in the range of temperature [100 – 300] K for isotopically enriched diamond samples. In this range of temperatures, the lattice thermal conductivity shows a high sensitivity to the isotopic enrichment and our calculations suggest that by growing more enriched diamond samples it is possible to achieve values of thermal conductivity up to three times larger than the commonly observed in isotopically enriched diamond samples with 99.93%  $C^{12}$  and 0.07  $C^{13}$ .

## VII. ACKNOWLEDGMENTS

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## Appendix A: Properties of matrix **A**

It is easy to prove that the matrix **A** is symmetric  $A_{\nu,\nu'} = A_{\nu',\nu}$  by using the properties:  $P_{\nu,\nu'}^{\nu''} = P_{\nu',\nu}^{\nu''}$  and  $P_{\nu,\nu'}^{\text{isot}} = P_{\nu',\nu}^{\text{isot}}$  in the definition of  $A_{\nu,\nu'}$  given in Eq.13. It is also possible to prove that it is positive semi-definite. In order to show that, the matrix **A** in Eq.13 can be

written as:

$$\mathbf{A} = \sum_{\nu, \nu'} P_{\nu, \nu'}^{\nu''} \mathbf{D}_{\nu, \nu'}^{\nu''} + \sum_{\nu, \nu'} P_{\nu, \nu'}^{\text{isot}} \mathbf{D}_{\nu, \nu'} + \sum_{\nu} P_{\nu}^{\text{be}} \mathbf{D}_{\nu} \quad (\text{A1})$$

where  $\mathbf{D}_{\nu, \nu'}^{\nu''}$  is a matrix with all the element equal to zero apart those involving the triplets  $\{\nu, \nu', \nu''\}$

$$\mathbf{D}_{\nu, \nu'}^{\nu''} = \begin{matrix} & \nu & \nu' & \nu'' \\ \begin{matrix} \nu \\ \nu' \\ \nu'' \end{matrix} & \begin{pmatrix} 1 & 1 & -1 \\ 1 & 1 & -1 \\ -1 & -1 & 1 \end{pmatrix} \end{matrix} \quad (\text{A2})$$

whose eigenvalues are: 0, 0 and 3.

For the part representing the elastic scattering with the isotopes:  $\mathbf{D}_{\nu, \nu'}$  is a matrix with all the elements equal to zero apart those involving the couples  $\{\nu, \nu'\}$

$$\mathbf{D}_{\nu, \nu'} = \begin{matrix} & \nu & \nu' \\ \begin{matrix} \nu \\ \nu' \end{matrix} & \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \end{matrix} \quad (\text{A3})$$

with eigenvalues 0 and 2.

Finally for the border effect,  $\mathbf{D}_{\nu}$  is a matrix with all the elements equal to zero apart those involving  $\{\nu, \nu\}$

$$\mathbf{D}_{\nu} = \begin{matrix} & \nu \\ \nu & (1) \end{matrix} \quad (\text{A4})$$

Since  $P_{\nu, \nu'}^{\nu''}$ ,  $P_{\nu, \nu'}^{\text{isot}}$  and  $P_{\nu}^{\text{be}}$ , are non negative then the total matrix is positive semi-definite because sum of positive semi-definite matrices.

## Appendix B: Phonon relaxation times

When different events of scattering are present such as anharmonic scattering, scattering with isotopic impurities and border effects the total phonon relaxation time  $\tau_{\mathbf{q}j}^T$  is expressed by the Matthiessen's rule as:

$$(\tau_{\mathbf{q}j}^T)^{-1} = (\tau_{\mathbf{q}j})^{-1} + (\tau_{\mathbf{q}j}^{\text{be}})^{-1} + (\tau_{\mathbf{q}j}^{\text{isot}})^{-1} \quad (\text{B1})$$

where:

$$\begin{aligned} (\tau_{\mathbf{q}j})^{-1} &= 2\Gamma_{\mathbf{q}j} = \frac{\pi}{\hbar^2 N_0} \sum_{\mathbf{q}'j', \mathbf{q}''j''} |V^{(3)}(\mathbf{q}j, \mathbf{q}'j', \mathbf{q}''j'')|^2 \\ &\times \left[ 2(\bar{n}_{\mathbf{q}'j'} - \bar{n}_{\mathbf{q}''j''})\delta(\hbar\omega_{\mathbf{q}s} + \hbar\omega_{\mathbf{q}'j'} - \hbar\omega_{\mathbf{q}''j''}) + \right. \\ &\left. (1 + \bar{n}_{\mathbf{q}'j'} + \bar{n}_{\mathbf{q}''j''})\delta(\hbar\omega_{\mathbf{q}j} - \hbar\omega_{\mathbf{q}'j'} - \hbar\omega_{\mathbf{q}''j''}) \right] \quad (\text{B2}) \end{aligned}$$

is the relaxation time due to the anharmonic scattering processes with  $\Gamma_{\mathbf{q}j}$  half width at half maximum of the corresponding phonon broadening; while

$$(\tau_{\mathbf{q}j}^{\text{be}})^{-1} = \frac{c_{\mathbf{q}j}}{LF} \quad (\text{B3})$$

is the relaxation time due to the border effects and

$$(\tau_{\mathbf{q}j}^{\text{isot}})^{-1} = \frac{\pi}{2N_0} \omega_{\mathbf{q}j}^2 \sum_{\mathbf{q}'j'} \delta(\hbar\omega_{\mathbf{q}j} - \hbar\omega_{\mathbf{q}'j'}) \sum_s g_2^s \left| \sum_{\alpha} z_{\mathbf{q}j}^{s\alpha*} z_{\mathbf{q}'j'}^{s\alpha} \right|^2 \quad (\text{B4})$$

the relaxation time associated to the elastic scattering with isotopic impurities.

## Appendix C: Conjugate gradient method

The conjugate gradient minimization<sup>25</sup> of Eq.23 or Eq. 26 requires the evaluation of the gradient  $\mathbf{g}_i = \mathbf{A}\mathbf{f}_i - \mathbf{b}$  and a line minimization. Since the form is quadratic the line minimization can be done analytically and exactly. Moreover the information required by the line minimization at iteration  $i$  can be recycled to compute the gradient at the next iteration  $i + 1$ . Starting with an the initial vector  $\mathbf{f}_0 = \mathbf{f}^{\text{SMA}}$ , initial gradient  $\mathbf{g}_0 = \mathbf{A}\mathbf{f}_0 - \mathbf{f}^{\text{SMA}}$  and letting  $\mathbf{h}_0 = -\mathbf{g}_0$ , the conjugate gradient method can be summarized with the recurrence:

$$\mathbf{t}_i = \mathbf{A}\mathbf{h}_i \quad (\text{C1})$$

$$\mathbf{f}_{i+1} = \mathbf{f}_i - \frac{\mathbf{g}_i \cdot \mathbf{h}_i}{\mathbf{h}_i \cdot \mathbf{t}_i} \mathbf{h}_i \quad (\text{C2})$$

$$\mathbf{g}_{i+1} = \mathbf{g}_i - \frac{\mathbf{g}_i \cdot \mathbf{h}_i}{\mathbf{h}_i \cdot \mathbf{t}_i} \mathbf{t}_i \quad (\text{C3})$$

$$\mathbf{h}_{i+1} = -\mathbf{g}_{i+1} + \frac{\mathbf{g}_{i+1} \cdot \mathbf{g}_{i+1}}{\mathbf{g}_i \cdot \mathbf{g}_i} \mathbf{h}_i \quad (\text{C4})$$

where  $\mathbf{h}_i$  is the search direction and  $\mathbf{t}_i$  is an auxiliary vector. Notice that each iteration requires only one application of the matrix  $\mathbf{A}$  on the vector  $\mathbf{h}_i$  as in the OS method. This is the computationally more demanding part of the conjugate gradient step.

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